Pumice-catalyzed ozonation degradation of *p*-chloronitrobenzene in aqueous solution

Lei Yuan [a,b], Jimin Shen [a], Zhonglin Chen [a,*], Yu Liu [a]

[a] *State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin, 150090, China*
[b] *Institute of Natural Resources and Ecology, Heilongjiang Academy of Science, Harbin, 150040, China*

ABSTRACT

The use of pumice for heterogeneous catalytic ozonation significantly enhances the degradation efficiency and the total organic carbon (TOC) removal of *p*-chloronitrobenzene (*p*CNB) in aqueous solution compared with ozonation alone because of the synergistic effect between ozone and the catalyst. The *p*CNB adsorption was too small to contribute significantly to the *p*CNB degradation during pumice-catalyzed ozonation. The decomposition rate of the aqueous ozone increased 1.374-fold in the presence of pumice. High pH also positively affected the pumice-catalyzed ozonation, as nearly uncharged surfaces (the solution pH was close to the point of zero charge) are favorable for catalytic *p*CNB ozonation. *tert*-Butanol remarkably decreases the removal efficiency of catalytic *p*CNB ozonation, which suggests that *p*CNB degradation follows the mechanism of hydroxyl radical oxidation. Increasing both the pumice and ozone concentrations enhanced the removal effectiveness of *p*CNB. Pumice is an efficient green catalyst for *p*CNB degradation in aqueous solution.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, heterogeneous catalytic ozonation has received much attention in the field of water treatment because of its high oxidation potential. Several studies have been reported on the degradation of organic pollutants in aqueous solution through ozonation with heterogeneous catalysts, such as cobalt hydroxide [1], manganese silicate [2], and non-polar bonded alumina [3]. These metallic oxide catalysts significantly enhance the degradation efficiency of organic pollutants compared with ozonation alone. In the systems mentioned above, the degradation of organic pollutants mostly follows the hydroxyl radical (•OH) oxidation mechanism. Moreover, water treatment catalysts are limited by their high cost and reuse. Thus, alternative catalysts should be investigated. Consequently, low cost natural solid minerals, such as sand, soil, zeolite, alumina oxide, and goethite, have been recently used in the heterogeneous ozonation of toxic organic pollutants [4–10]. Pumice is a porous, natural glass formed from volcanic activity and contains relatively high concentrations of silica, aluminum, and iron. Pumice has been used as adsorbent and as photocatalysts in water treatment [11–14]. It was selected as the catalyst in the present study because of its excellent chemical

and configurable properties, such as high mechanical strength and chemical stability. *p*-Chloronitrobenzene (*p*CNB) is widely used in the production of pesticide, herbicide, dyes, lumber preservatives, pharmaceuticals, photograph films, antioxidants, gasoline additives, and other industrial chemicals. The reaction rate constant of *p*CNB with •OH is $2.6 \times 10^9 \, \text{M}^{-1} \, \text{s}^{-1}$, whereas that with ozone alone is only $1.6 \, \text{M}^{-1} \, \text{s}^{-1}$, suggesting that *p*CNB scarcely reacts with molecular ozone [15]. In addition, *p*CNB is toxic and is not readily biodegraded. As a special indicator of •OH, *p*CNB was chosen as the target organic compound given its refractory nature in conventional chemical oxidation. The primary objectives of the present study are to apply pumice catalyst in ozonation system, to investigate the degradation efficiency of refractory organic compounds in the presence of catalysts in aqueous solution, to confirm preliminarily the reaction mechanism, and to explore pumice stability in catalyzed ozonation processes.

2. Experimental

2.1. Materials and reagents

A 100 mg/L stock solution of *p*CNB (99.5% purity, Chem Service, USA) was prepared and stored in an amber flask. Milli-Q ultrapure water (specific resistance $\geq 18 \, \text{M}\Omega \, \text{cm}$) was used throughout these experiments. *tert*-Butanol (Shandong Ruixing Chemical Factory, China) was used without further purification. Perchloric acid (Tianjin Dongli Chemical Factory, China) and sodium hydroxide

(Harbin Xinchun Chemical Factory, China) were added in aqueous solution to control the pH. Diluted sodium thiosulfate solution was used for quenching the reaction. All other chemicals used in the experiments were analytical grade reagents. All glasswares except for volumetric flasks were muffled overnight at 673 K. The volumetric flasks were washed by soaking in chromic acid and then rinsing with redistilled water. Natural pumice (Wudalianchi, China, diameter 0.6–0.8 mm) was used as the catalyst. The pumice blocks were cleaned before the catalytic ozonation process by ultrasonication for 10 min in a vessel of redistilled water. Afterwards, they were dried overnight in an oven at 333 K, and then stored in a dry vacuum oven before use.

2.2. Experimental procedure

The catalytic activity experiments were performed in a 1.2 L flat-bottomed flask as the reactor vessel. The ozone was generated from pure oxygen by an ozone generator (DHX-SS-1G, Harbin Jiu-Jiu Electrochemistry Engineering Ltd., China). Ultrapure water (1 L), with pH pre-adjusted with aqueous solutions of sodium hydroxide or perchloric acid, was transferred into the reactor. Using a silicon dispenser, ozone was bubbled into the reactor to the desired concentration. Then, the catalyst (1.0 g) and stock *p*CNB solution (1 mL) were immediately dosed into the reactor to achieve concentrations of 1.0 g/L and 100 μg/L, respectively. A magnetic stirrer was used to achieve sufficient mixing of the ozone solution with the catalyst and stock *p*CNB solution. The reaction temperature was maintained at 296 K using a thermostated water bath. Samples (50 mL) were taken at specific time intervals (0, 1, 5, 10, and 20 min), and the residual ozone was instantly quenched with 0.1 mL of aqueous sodium thiosulfate solution (0.1 mol/L). The quenched samples were then analyzed through liquid chromatography for *p*CNB quantification.

2.3. Analytical method

The residual ozone concentration in the aqueous solution was determined via spectrophotometry using the indigo method [16]. The *p*CNB concentration was determined using a liquid chromatograph (HPLC, LC-1200, Agilent, USA) with UV detection at 265 nm. The separation was performed with a Venusil Mp-C18 column (150 mm × 4.6 mm, 5 μm, Agela Technologies Inc.) by isocratic elution with 80% water and 20% methanol at a flow rate of 1.0 mL/min. The practical method detection limit was 0.1 μg/L. The pH of aqueous solution was measured by a PB-10 pH meter (Sartorious, Germany). An electron paramagnetic resonance (EPR, EMX-8/2.7 ESR spectrometer with ER4102ST cavity, Bruker, Germany) experiment was conducted to determine the •OH generated during the ozone decomposition process. The *p*CNB mineralization was monitored via total organic carbon (TOC) removal, which was determined using a TOC analyzer (TOC-V$_{CPH}$, Shimadzu, Japan).

X-ray fluorescence spectroscopy (XRF, AXIOS-PW 4400, PANalytical, Holand) was used to analyze the chemical composition of the catalyst. Physical properties of the catalyst samples were measured according to the Brunauer–Emmet–Teller (BET) method with krypton adsorption at liquid nitrogen temperature on a surface area and porosity analyzer (Micromeritics ASAP 2020, USA). A special test tube was needed to host the sample to measure the BET specific surface area of the catalyst. The density of the surface hydroxyl groups was measured according to the saturated deprotonation method described by Tamura et al. [17] and elsewhere [18]. The point of zero charge (pH$_{PZC}$) was measured using a mass titration method [19,20]. An inductively coupled plasma emission spectrometer (ICP, Optima 5300DV, PerkinElmer, USA) was used to determine the metal ion concentrations in aqueous solution.
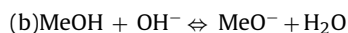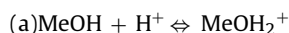
Table 1
Physical properties of pumice.

Parameter	Value
BET surface area (m^2/g)	1.805
Pore volume (cm^3/g)	0.004
Pore size (nm)	12.16

3. Results and discussion

3.1. Catalysts characterization

Given the significant role of heterogeneous catalyst on the catalytic ozonation of gas–liquid–solid phases, the surface characteristics of the pumice catalyst were investigated in the experiment. The XRF analysis revealed that natural pumice is composed mainly of SiO$_2$ (49.79%) and Al$_2$O$_3$ (15.6%) followed by Fe$_2$O$_3$ (9.15%), K$_2$O (5.31%), MgO (4.15%), Na$_2$O (4.05%), and TiO$_2$ (3.13%). In the presence of aqueous solution, surface hydroxyl groups are developed on these oxides. The results show that 0.27 mmol/g surface hydroxyl groups were present on the surface of the pumice catalyst. Hydroxyl groups formed on metal oxide surfaces behave as Brönsted acid sites. Specifically, the surface hydroxyl groups on the heterogeneous catalytic surface are believed to be crucial for the initiation of •OH from the decomposition of ozone [21]. These hydroxyl groups exhibit pH-dependent charges in aqueous solution. The respective densities of these functional groups are influenced by the solution pH. At pH < pH$_{pzc}$ (6.22), the surface hydroxyl groups on metal oxides are in their protonated form (a), and when pH > pH$_{pzc}$, they are in their deprotonated form (b) [22], as shown below:

$$(a) MeOH + H^+ \Leftrightarrow MeOH_2^+$$

$$(b) MeOH + OH^- \Leftrightarrow MeO^- + H_2O$$

where Me—OH, Me—OH$_2^+$, and Me—O$^-$ represent neutral, protonated, and deprotonated surface hydroxyl groups, respectively. Furthermore, physical properties of pumice were evaluated using the BET method, as shown in Table 1.

3.2. Degradation efficiency of pCNB in the different processes

The degradation of the 100 μg/L *p*CNB in aqueous solution was performed using ozonation alone, ozonation/pumice, and adsorption onto pumice. Fig. 1 shows the variation of the *p*CNB
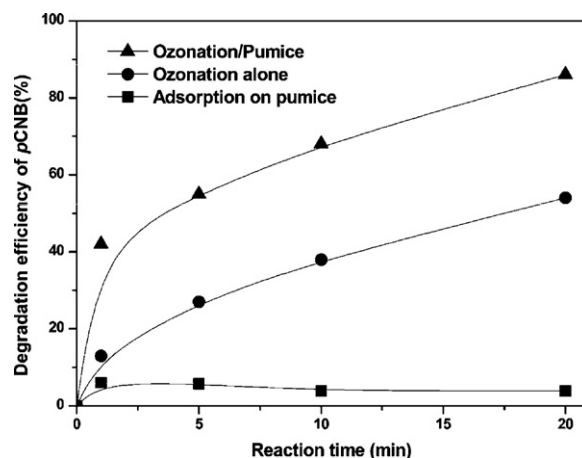

Fig. 1. Degradation efficiency of *p*CNB in the different processes (reaction conditions: temperature 296 K; initial pH 6.86; initial *p*CNB concentration 100 μg/L; concentration of total applied ozone 0.6 mg/L; concentration of pumice used in the catalytic ozonation 1.0 g/L).
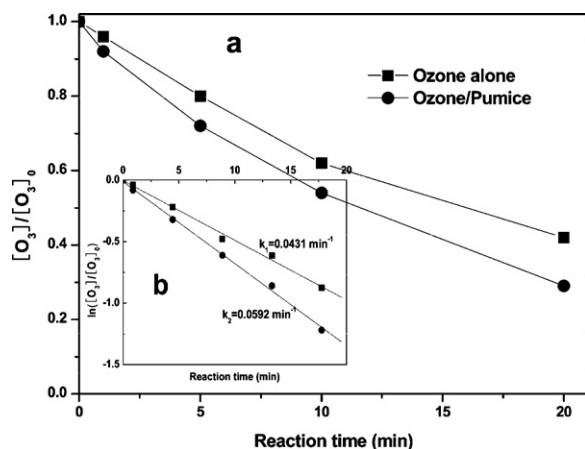
Fig. 2. Promotion of ozone decomposition in the different processes (reaction conditions: temperature 296 K; initial pH 6.86; concentration of total applied ozone 0.6 mg/L; concentration of pumice used in ozone decomposition 1.0 g/L).

concentration with reaction time under the three experimental conditions.

As shown in Fig. 1, the lowest *p*CNB degradation efficiency appears with adsorption on pumice, resulting in the removal of only 3.9% of the initial *p*CNB after 20 min. Compared with ozonation alone and that of the catalytic ozonation processes, the adsorption of *p*CNB is too small to contribute significantly to its degradation efficiency and can therefore be neglected. With the presence of ozone in the aqueous solution, the concentration of *p*CNB decreased with increasing reaction time. The presence of pumice catalyst significantly enhanced the degradation efficiency of *p*CNB, and the best result was obtained when pumice-catalyzed ozonation was used. Compared with the cumulative effect of ozonation alone and adsorption of pumice, an increment of approximately 26.5% of *p*CNB degradation was observed with the ozonation/pumice process. The experimental results suggest that the presence of the pumice catalyst has a synergistic effect with ozone for the degradation of *p*CNB.

3.3. Mechanism of catalytic ozonation

3.3.1. Promotion of ozone decomposition by pumice

Ozone is very unstable in aqueous solution because of its highly active resonance structures. The half-life of molecular ozone varies from a few seconds to a few minutes and depends on many factors [23]. The decomposition of ozone in aqueous solution at pH 6.86, both with and without pumice, was investigated to determine the role of pumice in dissolved ozone decomposition.

The decomposition behavior of water-dissolved ozone was investigated. Fig. 2a shows that the ozone decomposition efficiency in aqueous solution is greatly enhanced with pumice than in the ozone alone system at 296 K and a reaction time of 20 min. As shown in Fig. 2b, the ozone decomposition followed first-order kinetics both with and without pumice. The first-order decomposition of aqueous ozone was obviously enhanced in the presence of pumice, with its decomposition rate increasing 1.374-fold.

The current experiment determined •OH formation using spin-trapping/EPR technique, which can detect unstable radicals by measuring the intensity of the DMPO—OH adduct signal, during ozone alone and ozone/pumice. The results are summarized in Fig. 3. The spectra of the DMPO—OH adduct signal at different systems are all composed of quartet lines that have a peak height ratio of 1:2:2:1, and the parameters are the hyperfine constants $\alpha_N = 1.489$ mT, $\alpha_H = 1.489$ mT, and g-value = 2.0059. This experimental phenomenon indicates that •OH initiation occurs in
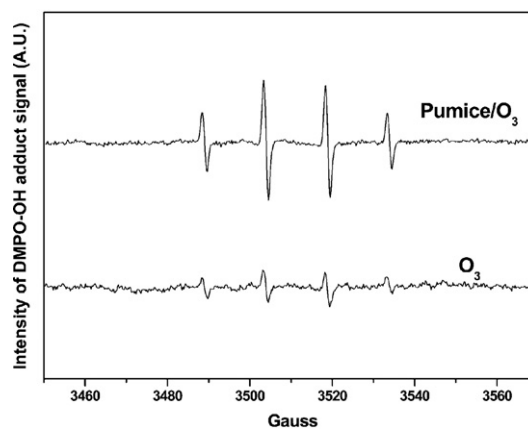

Fig. 3. Comparison of hydroxyl radicals captured by EPR under different systems.

the two processes mentioned above. Moreover, the DMPO—OH adduct signal observed in the catalytic ozone systems are stronger than in ozone alone. The results in Figs. 2 and 3 also suggest that the pumice-catalyzed ozone generates higher •OH concentrations under the same experimental conditions compared with that obtained from the ozone alone system. The reason for this finding is the introduction of a heterogeneous surface, which can significantly affect the ozone decomposition mechanism.

3.3.2. Influence of tert-butanol on degradation efficiency of pCNB

Experiments were performed to compare the *p*CNB degradation efficiency obtained in the presence of *tert*-butanol with that in its absence to identify preliminarily the reaction mechanism of *p*CNB degradation through ozonation alone and catalytic ozonation processes. *tert*-Butanol is a stronger radical scavenger, as indicated by its higher reaction rate constant with hydroxyl radicals ($k_{•OH} = 5 \times 10^8$ M^{-1} s^{-1}) [24] and with ozone alone ($k_{o_3} = 3 \times 10^{-3}$ M^{-1} s^{-1}) [25]. *tert*-Butanol reacts with •OH, generating inert intermediates, thus causing the termination of the radical chain reaction. Therefore, *tert*-butanol is a more suitable indicator for the radical type reaction because of its stronger scavenging effect on •OH. *tert*-Butanol was used to perform the preliminary test on the catalyzed ozonation mechanism.

In Fig. 4, the presence of *tert*-butanol shows a very strong influence on the degradation of ozonation alone and pumice-catalyzed ozonation processes, causing a primary reduction in
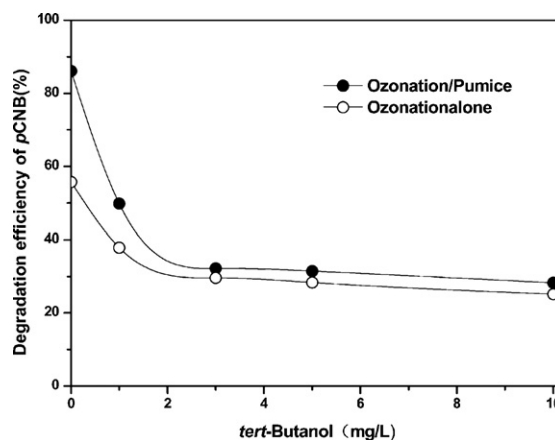

Fig. 4. Influence of *tert*-butanol on the *p*CNB degradation efficiency (reaction conditions: temperature 296 K; initial pH 6.86; initial *p*CNB concentration 100 μg/L; concentration of total applied ozone 0.6 mg/L; concentration of pumice used in catalytic ozonation 1.0 g/L; reaction time 20 min).

Fig. 5. Influence of initial pH on *p*CNB degradation efficiency (reaction conditions: temperature 296 K; initial *p*CNB concentration 100 μg/L; concentration of total applied ozone 0.6 mg/L; concentration of pumice used in catalytic ozonation 1.0 g/L; reaction time 20 min).
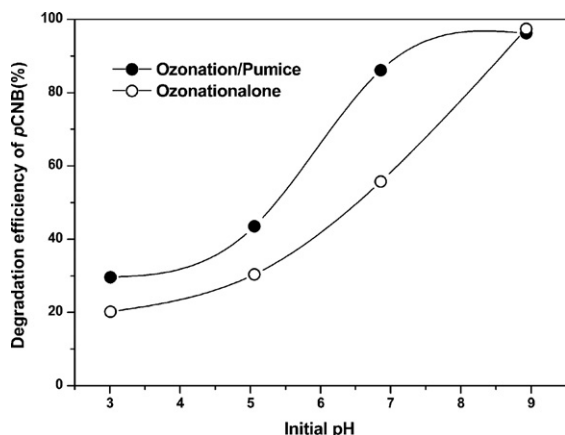

Fig. 6. Influence of ozone concentration on the degradation efficiency of *p*CNB (reaction conditions: temperature 296 K; initial pH 6.86; initial *p*CNB concentration 100 μg/L; concentration of pumice used in catalytic ozonation 1.0 g/L).

the degradation rate, even at a very low concentration (1.0 mg/L). Moreover, the *p*CNB degradation efficiency during ozonation alone decreased from 55.7% to 25.2%, and the degradation rate of the pumice-catalyzed ozonation dropped from 86.1% to 28.3%. Thus, the presence of *tert*-butanol effectively inhibits radical generation in the aqueous solution at pH 6.86. The experimental results indicate that the addition of *tert*-butanol at different concentrations negatively influence the *p*CNB degradation efficiency during both ozonation alone and pumice-catalyzed ozonation. This indicates that *tert*-butanol competitively traps and rapidly consumes •OH in aqueous solution. The results also suggest that in both ozonation alone and pumice-catalyzed ozonation, *p*CNB is primarily oxidized by •OH in aqueous solution.

3.4. Influence of variables on pCNB degradation efficiency

Several variables significantly influence the *p*CNB degradation efficiency in the ozonation experiments in the present study. These variables are very important in the practical operation of organic compound removal in wastewater treatment and drinking water supply from rivers and lakes. Therefore, the experiments preliminarily investigated the influence of variables on the *p*CNB degradation efficiency.

3.4.1. Initial pH

Solution pH reflects the OH⁻ concentration. The ozone decomposition rate increases with pH value, which promotes •OH formation. Thus, pH has a remarkable effect on ozone decomposition and the pumice catalytic ozonation process. The influence of initial pH on *p*CNB degradation efficiency in aqueous solution was investigated during ozonation alone and pumice-catalyzed ozonation. The results are shown in Fig. 5.

Fig. 5 shows that the degradation efficiency of *p*CNB in aqueous solution is greatly enhanced by increasing pH from 3.01 to 8.93 in the ozonation alone and pumice-catalyzed ozonation systems at a reaction temperature 296 K. The degradation efficiency of ozonation alone was 55.7%, and that of the pumice-catalyzed ozonation system was 86.1% (pH 6.86). However, when the pH solution was decreased to 3.01 by adding perchloric acid, the degradation efficiency of ozonation alone and the pumice catalyzed ozonation system were reduced to 20.2% and 28.3%, respectively. In contrast, when the pH of the solution was raised to 8.93, regulated with sodium hydroxide, the degradation rate of ozonation alone increased to 97.4%. Under the same experimental conditions, the degradation rate of the pumice-catalyzed ozonation system was
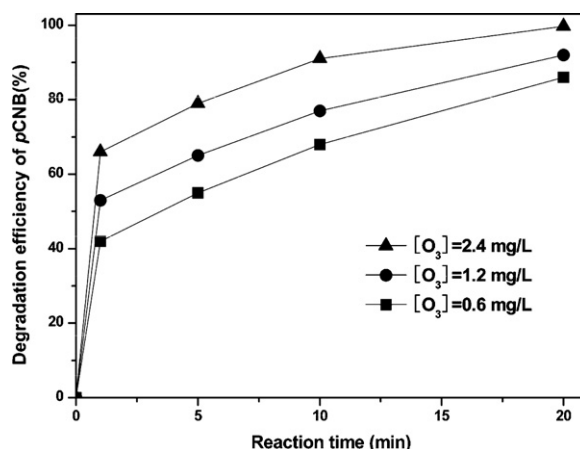
96.2%. Fig. 5 shows that the higher the solution pH, the higher the degradation rate observed. When the solution pH was near the pH_pzc of pumice, remarkable activity was observed in the catalyzed ozonation process, wherein the relative •OH concentration was much higher than in the ozonation alone process.

3.4.2. Ozone concentration

The heterogeneous catalytic ozonation of *p*CNB in aqueous solution is a reaction system of gas–liquid–solid phases, in which the ozone concentration is a crucial factor that affects the degradation efficiency. The experiments were performed by varying the ozone concentration from 0.6 mg/L to 2.4 mg/L. Fig. 6 shows the influence of ozone concentration on the effectiveness of *p*CNB removal as a function of reaction time. The ozone concentration positively influenced the effectiveness of *p*CNB removal. When the ozone concentration was increased from 0.6 mg/L to 2.4 mg/L, the removal effectiveness of *p*CNB in the catalytic ozonation increased from 86.1% to 99.7% within 20 min. This enhancement of the removal effectiveness may be caused by the generation of more •OH.

3.4.3. Catalyst concentration

The catalyst concentration is an important parameter in catalytic ozonation. The effect of increasing the catalyst concentration from 0.5 g/L to 2 g/L on the degradation of *p*CNB was analyzed. Fig. 7 shows the effect of various catalyst concentrations on the removal
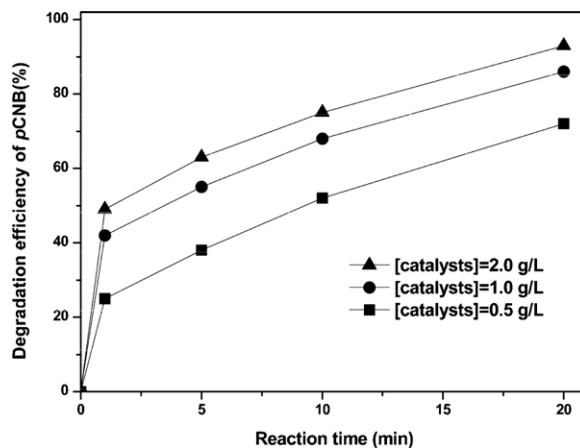

Fig. 7. Influence of catalyst concentration on *p*CNB degradation efficiency (reaction conditions: temperature 296 K; initial pH 6.86; initial *p*CNB concentration 100 μg/L; concentration of total applied ozone 0.6 mg/L).
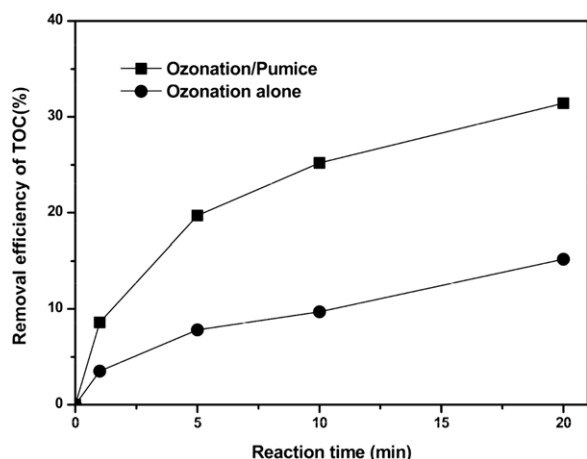
Fig. 8. Comparison of TOC removal efficiency (reaction conditions: temperature 296 K; initial pH 6.86; initial pCNB concentration 100 μg/L; the concentration of total applied ozone 0.6 mg/L; and concentration of pumice used in catalytic ozonation 1.0 g/L).

effectiveness of pCNB by catalytic ozonation. The catalyst concentrations exert an appreciable positive influence on the removal rate. These results demonstrate the effectiveness of pumice as a catalyst in catalyzed ozonation. The removal effectiveness of pCNB was enhanced by increasing the pumice concentration. Higher catalyst concentrations result in more active sites for catalytic reaction. The increase in active sites is accounted for in the removal of the organic pollutant.

3.5. Removal efficiency of TOC in the different processes

Given the significance of organic compound mineralization, experiments were performed to detect the removal efficiency of TOC during ozonation alone and pumice-catalyzed ozonation. The results are illustrated in Fig. 8.

Fig. 8 indicates that catalytic ozonation is more effective than ozonation alone in removing TOC from aqueous solution containing pCNB. Catalytic ozonation degraded 31.4% of the initial TOC compared with 15.2% by ozonation alone with the same total ozone applied (0.6 mg/L, reaction time 20 min). Furthermore, comparison of Fig. 8 (removal efficiency of TOC) and Fig. 1 (degradation efficiency of pCNB) shows that the removal of TOC is always lower than the disappearance of pCNB in the same process. This indicates that only part of the pCNB was mineralized into carbon dioxide and water, and that the byproducts were formed via the degradation of the initial compound in the selected processes. The degradation products of pCNB by ozonation may be low molecular carboxylic acids aside from carbon dioxide and water.

3.6. Catalyst stability of pumice for the degradation of pCNB

3.6.1. Recycling of pumice in catalyzed ozonation

The stability of the pumice catalyst was investigated by reusing one sample of catalyst in 10 successive ozonation experiments. At the end of each catalytic ozonation process, the insoluble catalyst was isolated and then rinsed gently with boiled Milli-Q ultrapure water. The catalysts were dried in an oven at 333 K, and then stored in a dry vacuum oven for use in the next ozonation experiment. The variation in the removal effectiveness of pCNB in the catalyzed ozonation was minimal, as shown in Table 2. When pumice was reused 10 times, the degradation efficiency and TOC removal of pCNB in aqueous solutions were 80.6% and 30.8%, respectively. The results indicate that the activity of pumice is relatively stable.

Table 2
Recycling of pumice in catalyzed ozonation.[a]

Recycling times	pCNB removal (%)	TOC removal (%)
1	84.3	31.5
2	85.2	30.7
5	82.2	31.3
8	84.5	32.4
10	80.6	30.8

[a] Reaction conditions: T = 296 K; pH = 6.86; [pCNB] = 100 μg/L; [O_3] = 0.6 mg/L; [catalyst] = 1.0 g/L.
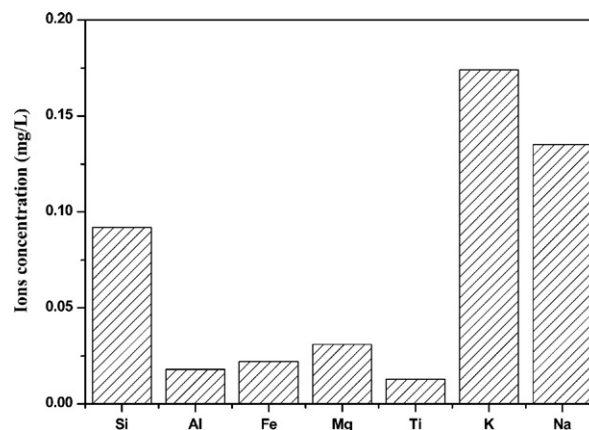

Fig. 9. Ions released into the catalyzed ozonation process (reaction conditions: temperature 296 K; initial pH 6.86; initial pCNB concentration 100 μg/L; concentration of total applied ozone 0.6 mg/L; concentration of pumice used in catalytic ozonation 1.0 g/L; reaction time 20 min).

Further studies shall investigate the surface structure, the real lifetime, and the method of the regeneration of pumice catalysts.

3.6.2. Ion release in catalyzed ozonation process

Based on the XRF analysis, the elemental composition of natural pumice are O, Si, Al, Fe, K, Mg, Na, and Ti. Additionally, the residual ion concentration in drinking water affects human health. Therefore, ions released into the catalyzed ozonation process are of particular concern. Fig. 9 shows the residual ion concentration after the catalyzed ozonation, and indicates the dissolution of ions after the catalyzed ozonation. However, the residual ion concentration was minimal. This residual ion concentration level is not dangerous to human health because it is lower than the criterion for drinking water in China. Therefore, the application of pumice-catalyzed ozonation in drinking water treatment is feasible.

4. Conclusions

Pumice is a useful catalyst for the decomposition of aqueous ozone and the heterogeneous ozonation of trace pCNB concentrations in aqueous solution. The addition of pumice increases the decomposition efficiency of ozone in aqueous solution compared with that of ozone alone. The presence of pumice catalyst significantly increases the degradation efficiency and the TOC removal of pCNB compared with that of ozonation alone. Moreover, high pH positively affects the pumice-catalyzed ozonation, as the nearly zero charged surfaces were favorable for the catalytic ozonation of pCNB. The degradation of pCNB in the ozonation and pumice-catalyzed ozonation processes followed the mechanism for hydroxyl radical oxidization. From a practical point of view, pumice shows promise for use in water treatment because it retains its catalytic activity for up to 10 successive cycles and the residual ion content was minimal after catalytic ozonation.

Acknowledgments

References

[1] Z.Z. Xu, Z.L. Chen, C. Joll, Y. Ben, J.M. Shen, H. Tao, Catal. Commun. 10 (2009) 1221–1225.
[2] Y. Liu, J.M. Shen, Z.L. Chen, Y. Liu, Desalination 279 (2011) 219–224.
[3] F. Erol, T.A. Özbelge, Chem. Eng. J. 139 (2008) 272–283.
[4] H. Choi, Y. Kim, H. Lim, J. Cho, J. Kang, K. Kim, Water Sci. Technol. 43 (2001) 349–356.
[5] H. Lim, H. Choi, T. Hwang, J. Kang, Water Res. 36 (2002) 219–229.
[6] Q. Fei, B.B. Xu, Z.L. Chen, J. Ma, D.Z. Sun, L.Q. Zhang, F.C. Wu, J. Hazard. Mater. 168 (2009) 246–252.
[7] M. Ernst, F. Lurot, J.C. Schorotter, Appl. Catal. B: Environ. 47 (2004) 15–25.
[8] H. Fujita, J. Izumi, M. Sagehashi, T. Fujii, A. Sakoda, Water Res. 38 (2004) 159–165.
[9] H. Fujita, J. Izumi, M. Sagehashi, T. Fujii, A. Sakoda, Water Res. 38 (2004) 166–172.
[10] J. Park, H. Choi, K. Ahn, J. Kang, Ozone Sci. Eng. 26 (2004) 141–151.
[11] S.S. Kaplan Bekaroglu, N.O. Yigit, T. Karanfil, M. Kitis, J. Hazard. Mater. 183 (2010) 389–394.
[12] M. Yavuz, F. Gode, E. Pehlivan, S. Ozmert, Y.C. Sharma, Chem. Eng. J. 137 (2008) 453–461.
[13] K. Venkata Subba Rao, M. Subrahmanyam, P. Boule, Appl. Catal. B: Environ. 49 (2004) 239–249.
[14] K. Venkata Subba Rao, A. Rachel, M. Subrahmanyam, P. Boule, Appl. Catal. B: Environ. 46 (2003) 77–85.
[15] J.M. Shen, Z.L. Chen, Z.Z. Xu, X.Y. Li, B.B. Xu, F. Qi, J. Hazard. Mater. 152 (2008) 1325–1331.
[16] H. Bader, J. Hoigné, Water Res. 15 (1981) 449–456.
[17] H. Tamura, A. Tanaka, K.Y. Mita, R. Furuichi, J. Colloid Interface Sci. 209 (1999) 225–231.
[18] E. Laiti, L.O. Öhman, J. Nordin, S. Sjöberg, J. Colloid Interface Sci. 175 (1995) 230–238.
[19] J.S. Noh, J.A. Schwarz, J. Colloid Interface Sci. 130 (1989) 157–164.
[20] J.S. Noh, J.A. Schwarz, Carbon 28 (1990) 675–682.
[21] J. Ma, N.J.D Graham, Water Res. 33 (1999) 785–793.
[22] L. Zhao, J. Ma, Z.Z. Sun, H.L. Liu, Environ. Sci. Technol. 43 (2009) 2047–2053.
[23] B. Kasprzyk-Hordern, M. Ziólek, J. Nawrocki, Appl. Catal. B: Environ. 46 (2003) 639–669.
[24] G. Bablon, W.D. Bellamy, M.M. Bourbigot, in: B. Langlais, D.A. Reckhow, D.R. Brink (Eds.), Ozone in Water Treatment: Application and Engineering, Lewis Publishers, Chelsea, Michigan, USA, 1991, pp. pp11–pp132.
[25] J. Hoigné, H. Bader, Water Res. 17 (1983) 173–183.